

MENU**SEARCH****INDEX****DETAIL****JAPANESE****LEGAL
STATUS**

1 / 1

PATENT ABSTRACTS OF JAPAN(11)Publication number : **2004-055139**(43)Date of publication of
application : **19.02.2004**

(51)Int.Cl.

H01M 4/58**H01M 4/02****H01M 10/40**(21)Application
number : **2002-206582**(71)
Applicant : **HITACHI CHEM CO LTD**(22)Date of filing : **16.07.2002**(72)Inventor : **ISHII YOSHITO
SUDA SOICHIRO
NISHIDA TATSUYA****(54) NEGATIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY, AND LITHIUM SECONDARY BATTERY**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode suitable for a lithium secondary battery with little deterioration in a boosting charge and discharge characteristic and a cycle characteristic when a negative electrode density is raised, and a high capacity lithium secondary battery with improved energy density per volume of the secondary battery.

SOLUTION: The negative electrode for the lithium secondary battery is comprised by pressurizing and integrating a collector and a mixture of graphite particles and an organic binding agent. It is characterized by that a diffraction intensity ratio (002)/(110) measured by X-ray diffraction of the negative electrode is ≤ 500 , and it has a positive electrode including the negative electrode for the lithium secondary battery and a lithium compound.

JAPANESE

[JP,2004-055139,A]

Drawing selection

Drawing 1

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

**JPO and INPIT are not responsible for
any
damages caused by the use of this
translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]

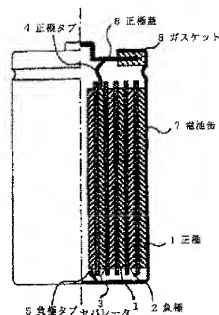
A negative electrode for lithium secondary batteries whose diffraction intensity ratio (002)/(110) measured by an X diffraction of this negative electrode in a negative electrode for lithium secondary batteries which a mixture and a charge collector of a graphite-grains child and an organic system binder are pressurized, and it comes to unify is less than 500.

[Claim 2]

The negative electrode for lithium secondary batteries according to claim 1 whose density of a mixture of a graphite-grains child and an organic system binder is $1.45 - 1.95 \text{ g/cm}^3$.

[Claim 3]

The negative electrode for lithium secondary batteries according to claim 1 or 2 whose crystallite size L_c (002) of 1-100 micrometers and C shaft orientations of a crystal a graphite-grains child's mean particle diameter is 500 Å or more.



[Translation done.]

[Claim 4]

Claims 1-3 are the lithium secondary batteries which have a negative electrode for lithium secondary batteries of a statement, and an anode containing a lithium compound either.

[Translation done.]

JAPANESE

[JP,2004-055139,A]

Drawing selection **Drawing 1**

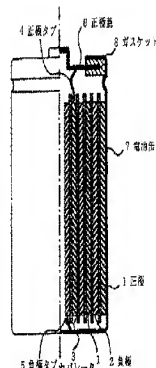
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.



[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the negative electrode for lithium secondary batteries, and a lithium secondary battery. It is related with the negative electrode for obtaining the lithium secondary battery suitable in more detail and it which are high capacity and were excellent in the rapid charging and discharging characteristic and the cycle characteristic to use for a portable device, an electromobile, stationary energy storage, etc., and its manufacturing method.

[0002]

[Description of the Prior Art]

The negative electrode of the conventional lithium secondary battery has the artificial-graphite particles which graphitized natural graphite particles, the artificial-graphite particles which graphitized corks, the organic system polymer material, the pitch, etc., for example, the graphite-grains child who ground these, the nodular graphite which graphitized mesophase carbon, etc. It mixes with an organic system binder and an organic solvent, and these graphite-grains children consider it as graphite paste, apply this graphite paste on the surface of copper foil, dry a solvent, and are used as a negative electrode for lithium secondary batteries. For example, as shown in JP,62-23433,B, the problem of the contents short circuit by the dendrite of lithium

is solved by using black lead for a negative electrode, and improvement of the cycle characteristic is aimed at.

[0003]

[Problem(s) to be Solved by the Invention]

However, in the associative strength between the layers of the crystal of C shaft orientations, since it is weak compared with combination of the plane direction of a crystal, combination between graphite layers goes out by grinding, and natural graphite with which graphite crystals are developed serves as what is called a lepidic graphite-grains child with a large aspect ratio. Since the aspect ratio of flaky graphite is large, when it kneads with a binder, it applies to a charge collector and an electrode is produced, Flaky graphite particles carry out orientation to the plane direction of a charge collector, and, as a result, charge-and-discharge capacity and a rapid charging and discharging characteristic not only fall easily, but, If negative-electrode density is carried out more than 1.45 g/cm^3 , there is not only a problem to which the destruction inside an electrode arises by expansion and contraction of C shaft orientations generated by repetition of the occlusion and discharge of lithium to graphite crystals, and a cycle characteristic falls, but, It becomes that it is hard to be emitted and occlusion and the problem to which the service capacity per weight of a rapid charging and discharging characteristic and a negative electrode and a cycle characteristic fall have lithium in negative-electrode black lead.

On the other hand, a lithium secondary battery is making negative-electrode density high, and can expect to enlarge the energy density per volume. Then, in order to raise the energy density per volume of a lithium secondary battery, when negative-electrode density is made high, the negative electrode with few falls is demanded of the rapid charging and discharging characteristic and the cycle characteristic.

[0004]

This invention provides the suitable negative electrode for the lithium secondary battery excellent in the rapid charging and discharging characteristic and the cycle characteristic in view of the above-mentioned problem, and provides the still more suitable negative electrode for a high capacity lithium secondary battery.

[0005]

[Means for Solving the Problem]

- (1) In a negative electrode for lithium secondary batteries which a mixture and a charge collector of a graphite-grains child and an organic system binder are pressurized, and it comes to unify, this invention relates to a negative electrode for lithium secondary batteries whose diffraction intensity ratio $(002)/(110)$ measured by an X diffraction of a negative electrode is less than 500.
- (2) This invention relates to a negative electrode for lithium secondary batteries of the aforementioned (1) statement whose density of a mixture of a graphite-grains child and an organic system binder is $1.45 - 1.95 \text{ g/cm}^3$.
- (3) This invention relates to a negative electrode for lithium secondary batteries the above (1) or given in (2) whose crystallite size $L_c(002)$ of 1-100 micrometers and C shaft orientations of a crystal a graphite-grains child's mean particle diameter is 500 Å or more.
- (4) -- further -- this invention -- aforementioned (1) - (3) -- either -- it is related with a lithium secondary battery which has a negative electrode for lithium secondary batteries of this invention of a statement, and an

anode containing a lithium compound.

[0006]

[Embodiment of the Invention]

The negative electrode for lithium secondary batteries of this invention is characterized by diffraction intensity ratio (002)/(110) measured by the X diffraction of said negative electrode pressurized and unified being less than 500 in the negative electrode for lithium secondary batteries which the mixture and charge collector of a graphite-grains child and an organic system binder are pressurized, and it comes to unify. said diffraction intensity ratio (002)/(110) -- desirable -- 10-500 -- more -- desirable -- 10-400 -- further -- desirable -- 10-300 -- it is especially considered as the range of 50-200 preferably. If diffraction intensity ratio (002)/(110) exceeds 500, the rapid charging and discharging characteristic and cycle characteristic of a lithium secondary battery to produce will fall.

Here diffraction intensity ratio (002)/(110) of the negative electrode for lithium secondary batteries, CuK -- alpha rays -- X -- a line source -- carrying out -- an X diffraction -- an angle of diffraction -- two -- theta -- = -- 26 - 27 -- a degree -- the neighborhood -- detecting -- having (002) -- a field -- a diffraction peak -- an angle of diffraction -- two -- theta -- = -- 70 - 80 -- a degree -- the neighborhood -- detecting -- having (110) -- a field -- a diffraction peak -- intensity -- from -- the following -- (-- one --) -- a formula -- it can ask .

(002) Field diffraction peak intensity / (110) field diffraction peak intensity (1) type

[0007]

In the negative electrode for lithium secondary batteries of this invention, it is preferred that the density of the mixture of the graphite-grains child and organic system binder which were pressurized and were united with the charge collector is 1.45 - 1.95 g/cm³. Said density has more preferred 1.5 - 1.9 g/cm³, its 1.6 - 1.85 g/cm³ is still more preferred, and especially its 1.65 - 1.8 g/cm³ is preferred. By making high density of the mixture of the graphite-grains child and binder in the negative electrode of this invention, the energy density per volume of the lithium secondary battery obtained using this negative electrode can be enlarged. The energy density per volume of the lithium secondary battery with which the density of the mixture of said graphite-grains child and an organic system binder is obtained by less than 1.45 g/cm³ becomes small. On the other hand, if the density of the mixture of said graphite-grains child and an organic system binder exceeds 1.95 g/cm³, the pouring-in nature of an electrolysis solution when producing a lithium secondary battery not only worsens, but the rapid charging and discharging characteristic and cycle characteristic of a lithium secondary battery to produce will fall easily.

The density of the mixture of this graphite-grains child after unification and a binder can be suitably adjusted with the clearance of devices, such as a pressure when carrying out unification shaping, and a roll press, etc., for example.

[0008]

As for the size Lc (002) of the microcrystal of C shaft orientations a graphite-grains child's crystal used by this invention, 500 Å or more is preferred, 800 Å or more is more preferred, and it is preferred that it is especially 1000-10000 Å. There is a tendency for service capacity to become small in less than 500 Å in the size Lc (002) of the microcrystal of C shaft orientations.

As for the interlaminar distance d of a graphite-grains child's crystal (002), 3.38 Å or less is preferred, it is more preferred that it is 3.37 Å or less, and it is still more preferred that it is 3.36 Å or less. When the

interlaminar distance d of a crystal (002) exceeds 3.38 Å, there is a tendency for service capacity to fall. Said L_c (002) and d (002) can be measured in X ray wide angle diffraction.

[0009]

The graphite-grains child who uses for the negative electrode for lithium secondary batteries of this invention, Although diffraction intensity ratio (002)/(110) measured by the X diffraction of the negative electrode after application of pressure and unification can be set to less than 500 and the black lead which should just have reformed particle shape for flaky graphite, nodular graphite, and flaky graphite by the mechanical process, and two or more materials can also be mixed and used, It is preferred to use the graphite-grains child of an aggregated particle who gathers or combined the primary particle of flat shape so that plurality and an orientation surface might serve as non parallel. In this invention, the particles of flat shape are shape which has a major axis and a minor axis, and a perfect not spherical thing is said. For example, the thing of shape, such as a lepidic form, the shape of a scale, and massive [a part of], is contained in this. In a graphite-grains child, the orientation surface of the particles of two or more flat shape with non parallel. The field and the state of gathering by using a near field as an orientation surface most level, without the particles of two or more flat shape gathering each orientation surface in the fixed direction if it puts in another way, and forming the graphite-grains child which it has in the shape of each particle and which carried out flat are said.

In the particles of this flat shape gathered or combined, particles with a mutual combination via the carbonaceous which carbonized binders, such as a pitch and tar, for example, If the state where it has joined together chemically is said and particles with a mutual set join together chemically, there is nothing, but it originates in the shape and the state where shape is maintained also as the aggregate also in the process in which a negative electrode is produced is said. From the field of mechanical intensity, a united thing is preferred.

[0010]

It is preferred that an aspect ratio is five or less, and the graphite-grains children who use it by this invention are more preferred if they are 1.2-5, if they are 1.2-3, they are still more preferred, and especially if they are 1.3-2.5, they are preferred. The thing as an aggregated particle which the aspect ratio made gather or combine two or more primary particles may be satisfactory for five or less graphite-grains child, and what changed shape may be satisfactory for him so that mechanical power may be applied and an aspect ratio may become five or less about one particle, and what was produced combining these may be satisfactory for him further.

When this aspect ratio exceeds 5, there is a tendency for the rapid charging and discharging characteristic and cycle characteristic of a lithium secondary battery which diffraction intensity ratio (002)/(110) measured by the X diffraction of the negative electrode after application of pressure and unification becomes large easily, and are acquired as a result to fall. By less than 1.2, this aspect ratio is in the tendency for the conductivity of the negative electrode to produce to fall, when the touch area between particles decreases.

In this invention, when the graphite-grains child who uses it exists as two or more aggregates or combination of particles, a graphite-grains child's primary particle means the particle unit accepted when it observes, for example with a scanning electron microscope (SEM) etc. An aggregated particle means the lump which this primary particle has gathered or combined.

An aspect ratio is expressed with A/B , when the length of the major axis direction of particles is set to A and

it sets minor-axis lay length to B. A graphite-grains child's aspect ratio in this invention expands a primary particle or the graphite-grains child of an aggregated particle under a microscope, chooses arbitrarily ten particles of the size whose length of a major axis is 10-50 micrometers, measures A/B, and takes the arithmetic mean value.

[0011]

In one secondary graphite-grains child, as a number which the primary particle of flat shape gathers or combines, it is preferred that they are three or more pieces, and if it is five or more pieces, it is more desirable. If it is 5-80 micrometers, it is more desirable, and if it is 5-50 micrometers, it is still more desirable, and it is preferred that a 1-100-micrometer particle is included with particle diameter as a size of the primary particle of each flat shape, and it is preferred that it is $2/3$ or less [of a secondary graphite-grains child's mean particle diameter which these gathered or combined]. As for the aspect ratio of the primary particle of each flat shape, 100 or less are preferred, 50 or less are more preferred, and 20 or less are still more preferred. As a desirable minimum of the aspect ratio of said primary particle, it is 1.2, and it is preferred that it is not spherical.

[0012]

The following [$8 \text{ m}^2/\text{g}$] have the preferred specific surface area of an aggregated particle, and the graphite-grains child in this invention is below $5 \text{ m}^2/\text{g}$ more preferably. If this graphite-grains child is used for a negative electrode, the rapid charging and discharging characteristic and cycle characteristic of a lithium secondary battery which are acquired can be raised, and irreversible capacity of the first cycle eye can be made small. When specific surface area exceeds $8 \text{ m}^2/\text{g}$, there is a tendency for the irreversible capacity of the first cycle eye of the lithium secondary battery obtained to become large, an energy density is low, and when producing a negative electrode further, it is in the tendency for many binders to be needed. As for the point whose rapid charging and discharging characteristic of the lithium secondary battery obtained, cycle characteristic, etc. are still better to specific surface area, it is still more preferred that it is $1.5\text{--}5 \text{ m}^2/\text{g}$, and it is preferred that it is especially $2\text{--}5 \text{ m}^2/\text{g}$. The measurement of specific surface area can take known methods, such as a BET adsorption method by nitrogen gas adsorption.

[0013]

Although there is no restriction in particular, the manufacturing method of the negative electrode for lithium secondary batteries of this invention. For example, mix the binder which can be graphitized at least and in which aggregate or black lead, and graphitization are possible, after grinding, mix and calcinate this grinding thing and 1 to 50 % of the weight of graphitized catalysts, obtain a graphite-grains child, and subsequently, After add an organic system binder and a solvent to this graphite-grains child, mixing to him, applying this mixture to a charge collector, drying and removing a solvent, it is producible by pressurizing and unifying.

[0014]

As aggregate which can be graphitized, although the carbide of corks powder and resin, etc. can be used, if it is the powder material which can be graphitized, there will be no restriction in particular, for example. Especially, the corks powder which are easy to graphitize, such as needle coke, is preferred. Although artificial-graphite powder etc. can be used as black lead in the end of natural graphite powder, for example, if powdered, there will be no restriction in particular. It is preferred that it is smaller than a graphite-grains child's particle diameter to produce, if 1-80 micrometers is more preferred and is $1\text{--}50$ micrometers in mean

particle diameter, it is still more preferred, and especially if the particle diameter of aggregate or black lead which can be graphitized is 5-50 micrometers, it is preferred. 1.2-500 are preferred, and if the ranges of it are 1.5-300, it is more preferred, if the ranges of it are 1.5-100, it is still more preferred, and especially if the ranges of the aspect ratio of aggregate or black lead which can be graphitized are 2-50, it is preferred. Aspect ratio measurement is performed by the same method as the above here. When the aspect ratio of aggregate or black lead which can be graphitized becomes large, there is a tendency for diffraction intensity ratio (002)/(110) measured by the X diffraction of the negative electrode after application of pressure and unification to become large, and there is a tendency for the service capacity per graphite-grains child weight to become small, by less than 1.2.

[0015]

As a binder, organic system materials, such as thermosetting resin, thermoplastics, etc. besides tar and a pitch, are preferred, for example. As for the loadings of a binder, it is preferred to add five to 80% of the weight to aggregate or black lead which can be graphitized, it is more preferred to add ten to 80% of the weight, it is still more preferred to add 20 to 80% of the weight, and especially its thing added 30 to 80% of the weight is preferred. There is a tendency for there to be too much quantity of a binder, or for a graphite-grains child's aspect ratio and specific surface area to produce to become large easily if too small. Although restriction in particular does not have a mixing method of aggregate or black lead which can be graphitized, and a binder, for example, it can be performed using a kneader etc., it is preferred to mix at the temperature more than the softening temperature of a binder. In the cases, such as a pitch and tar, 50-300 ** of a binder is specifically preferred, and when it is thermosetting resin, 20-180 ** is preferred.

[0016]

Next, the above-mentioned mixture is ground and this grinding thing and a graphitized catalyst are mixed. 1-100 micrometers is preferred, if it is 5-80 micrometers, it is more desirable, and if the particle diameter of this grinding thing is 5-50 micrometers, it is still more preferred and especially its 10-30 micrometers are preferred.

There is a tendency for a graphite-grains child's specific surface area which will be obtained if the particle diameter of this grinding thing exceeds 100 micrometers to become large, and there is a tendency for (002)/(110) ratio of a negative electrode obtained to become large, in less than 1 micrometer. It is preferred that it is 0.5 to 50 % of the weight, if it is 1 to 30 % of the weight, it is more preferred, and if the volatile matter content of this grinding thing is 5 to 20 % of the weight, it is still more preferred. Weight loss when measurement of volatile matter content heats this grinding thing for 10 minutes at 800 ** is called for. As a graphitized catalyst mixed with this grinding thing, if there is a function as a graphitized catalyst, there will be no restriction in particular, but the graphitized catalyst of metal, such as iron, nickel, titanium, silicon, and boron, these carbide, an oxide, etc. can be used, for example. In these, the compound of iron or silicon is preferred. As chemical structure of a compound, carbide is preferred. When the total amount of the grinding thing mixed with a graphitized catalyst and a graphitized catalyst is made into 100 % of the weight, its 1 to 50 % of the weight is preferred, if it is 5 to 30 % of the weight, it is more preferred, and if the addition of these graphitized catalysts is 7 to 20 % of the weight, it is still more preferred. A graphitized catalyst remains easily to the graphite-grains child who will produce if there is a tendency for specific surface area to become large and development of a graphite-grains child's crystal produced as the quantity of a graphitized catalyst is less than 1 % of the weight not only worsens, but it, on the other hand, exceeds 50 % of the weight. The

shape of powder is preferred, and the shape of powder whose mean particle diameter is 0.1-200 micrometers is preferred, and it is [the graphitized catalyst to be used is more preferred if it is 1-100 micrometers, and] more preferred [graphitized catalyst] if it is 1-50 micrometers.

[0017]

Next, although the above-mentioned mixture is calcinated and conducting graphitization treatment is performed, before calcinating, after fabricating said grinding thing and the mixture of a graphitized catalyst to specified shape with a press etc., it may calcinate. As for the compacting pressure in this case, about 1-300 MPa is preferred. As for calcination, it is preferred to calcinate on the conditions on which said mixture cannot oxidize easily, for example, the method of calcinating in a nitrogen atmosphere, argon atmosphere, a vacuum, and self-volatility atmosphere is mentioned. The temperature of graphitization is preferred, it is more preferred that it is not less than 2500 **, if it is not less than 2700 **, it is still more preferred, and it is preferred that it is especially 2800-3200 **. [of not less than 2000 **] When the temperature of graphitization is low, there is a tendency which remains easily to the graphite-grains child whom the graphitized catalyst added while development of the crystal of black lead was bad and there was a tendency for service capacity to become low produces. If it remains mostly in the graphite-grains child whom a graphitized catalyst produces, the service capacity per graphite-grains child weight will fall. When the temperature of graphitization is too high, black lead may sublime. When the molded product fabricated to specified shape with a press etc. performs calcination, Below its 1.65 g/cm³ is preferred, if it is below 1.55 g/cm³, it is more preferred, if it is below 1.50 g/cm³, it is still more preferred, and especially if the apparent density of the molded product after graphitization is below 1.45 g/cm³, it is preferred. There is a tendency for a graphite-grains child's specific surface area which the density of the molded product after graphitization produces above 1.65 g/cm³ to become large. The apparent density of the molded product after graphitization can be suitably adjusted with a pressure when fabricating to specified shape for example, with particle diameter, a press, etc. of the grinding thing mixed with said graphitized catalyst etc.

[0018]

Subsequently, although it grinds, a particle size is adjusted and it is considered as the graphite-grains child who is a negative electrode carbon material, as the grinding method, there is no restriction in particular, for example, impact crushing methods, such as a jet mill, a hammermill, and a pin mill, can be taken. As for the mean particle diameter of the negative electrode carbon material after grinding, 1-100 micrometers is preferred, its 5-50 micrometers are more preferred, and especially its 10-30 micrometers are preferred. It becomes easy to be possible [unevenness] for the surface of the negative electrode which will be produced if mean particle diameter becomes large too much, and there is a tendency to become easy to carry out the micro short circuit of the lithium secondary battery produced as a result, and for a cycle characteristic to fall. In this invention, mean particle diameter can be measured with a laser diffraction type particle-size-distribution meter.

[0019]

Said obtained graphite-grains child kneads with an organic system binder and a solvent, makes it paste state, and is fabricated by shape, such as a sheet shaped and a pellet type.

As an organic system binder, polyethylene, polypropylene, ethylene-propylene terpolymer, butadiene rubber, styrene butadiene rubber, isobutylene isoprene rubber, a high molecular compound with big ionic

conductivity, etc. can be used, for example.

[0020]

as a high molecular compound with said big ionic conductivity -- polyvinylidene fluoride, polyethylene oxide, polyepichlorohydrin, and poly -- face -- FAZEN, polyacrylonitrile, etc. can be used.

the mixing ratio of a carbon material and an organic system binder receives carbon material 100 weight section -- an organic system binder -- **** for 0.5 - 20 weight sections -- things are preferred.

[0021]

As a solvent, there is no restriction in particular and N-methyl-2-pyrrolidone, dimethylformamide, isopropanol, water, etc. are mentioned. In the case of the binder which uses water as a solvent, it is preferred to use a thickener together.

Restriction in particular does not have the quantity of a solvent, either, and it applies to a charge collector, and it pressurizes, unites with this charge collector, and let it be a negative electrode, after kneading a carbon material with an organic system binder and a solvent, producing a mixture and adjusting viscosity suitably.

As a charge collector, metal charge collectors, such as foil, such as nickel and copper, and a mesh, can be used, for example. Unification can be performed, for example with the molding method of a roll, a press, etc., and it may unify combining these. As for the pressure at this time of unifying, about 1-200 MPa is preferred.

[0022]

Thus, the obtained negative electrode is used for a lithium secondary battery. The lithium secondary battery of this invention is what has an anode containing a lithium compound and a negative electrode of said this invention, For example, it can obtain by arranging an anode and a negative electrode face to face via a separator, and pouring in an electrolysis solution, and this is excellent in a cycle characteristic and a rapid charging and discharging characteristic with high capacity as compared with the lithium secondary battery which uses the conventional negative electrode.

[0023]

there is no restriction in particular in the material, for example, independent in LiNiO_2 , LiCoO_2 , LiMn_2O_4 , etc., although the anode of the lithium secondary battery in this invention contains a lithium compound -- or it can be mixed and used.

A lithium secondary battery usually contains the electrolysis solution containing a lithium compound with an anode and a negative electrode.

As an electrolysis solution, LiClO_4 , LiPF_6 , LiAsF_6 , LiBF_4 , LiSO_3CF_3 , $\text{CH}_3\text{SO}_3\text{Li}$, Lithium salt, such as $\text{CF}_3\text{SO}_3\text{Li}$, for example Ethylene carbonate, Diethyl carbonate, dimethyl carbonate, methylethyl carbonate,

What is called organic electrolysis liquid melted into nonaqueous system solvents, such as propylene carbonate, acetonitrile, pro PIRONI tolyl, dimethoxyethane, a tetrahydrofuran, and gamma-butyrolactone, and a solid or what is called a gel polymer electrolyte can be used.

It is preferred to add a small amount of additive agents which show a decomposition reaction to an electrolysis solution at the time of the first time charge of a lithium secondary battery. Vinylene carbonate, biphenyl one, a propane sultone, etc. are raised as an additive agent, and 0.01 to 5 % of the weight is preferred as an addition.

As a separator, what combined the nonwoven fabric, the crossing, the fine hole film, or them which used

polyolefines, such as polyethylene and polypropylene, as the main ingredients, for example can be used. When it is made the structure in which the anode and negative electrode of the lithium secondary battery to produce do not carry out direct contact, it is not necessary to use a separator.

[0024]

The schematic diagram in transverse plane of a partial section of an example of a cylindrical lithium secondary battery is shown in [drawing 1](#). The anode 1 processed laminated and the negative electrode 2 processed similarly wind what was piled up via the separators 3, such as a micropore film made from polyethylene, and the cylindrical lithium secondary battery shown in [drawing 1](#) inserts this in the battery cans 7, such as metal, and is sealing-ized. The anode 1 is joined to the anode lid 6 via the positive electrode tab 4, and the negative electrode 2 is joined to the cell pars basilaris ossis occipitalis via the negative electrode tab 5. The anode lid 6 is being fixed to the battery can (positive electrode can) 7 with the gasket 8.

[0025]

[Example]

Hereafter, the example of this invention is described.

Example 1

Corks powder 50 weight section with a mean particle diameter of 10 micrometers and coal tar pitch 30 weight section were mixed at 230 °C for 2 hours. Subsequently, after grinding this mixture in mean particle diameter of 25 micrometers, this grinding thing 80 weight section and silicon carbide 20 weight section with a mean particle diameter of 25 micrometers were mixed with the blender, this mixture was put into the metallic mold, press forming was carried out by 100MPa, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 °C in a nitrogen atmosphere, it heat-treated at 3000 °C in a nitrogen atmosphere further, and the black lead Plastic solid was acquired. Furthermore this black lead Plastic solid was pulverized, and the graphite-grains child who is a negative electrode carbon material was obtained. The following measurement was performed from the obtained negative electrode carbon material. 1 The mean particle diameter by a laser diffraction type particle-size-distribution meter, 2 The specific surface area by a BET adsorption method, 3 An aspect ratio (average value for ten pieces), 4 The interlaminar distance d of the crystal by X ray wide angle diffraction (002), and 5 Crystallite size Lc (002) of C shaft orientations of a crystal. These measured value is shown in Table 1.

Mean particle diameter made the particle diameter in 50%D mean particle diameter using the laser diffraction size distribution measuring device (Shimadzu Corp. product name SALD-3000). Using X-ray diffractometer, the interlaminar distance d (002) monochrome-ized Cu-K alpha rays with nickel filter, and measured high purity silicon as a standard substance. Specific surface area computed the nitrogen absorption in liquid nitrogen temperature in accordance with measurement and a BET adsorption method using micromeritics product name ASAP 2010 by the multipoint method.

[0026]

Subsequently, by solid content, the organic system binder polyvinylidene fluoride (PVDF) which dissolved in N-methyl-2 pyrrolidone was added 10% of the weight to 90 % of the weight of obtained negative electrode carbon materials, was kneaded to them, and graphite paste was produced. This graphite paste was applied to 10-micrometer-thick rolled copper foil, further, it dried at 120 °C, N-methyl-2 pyrrolidone was removed, it compressed by 10MPa with a vertical press, and the sample electrode was obtained. 6 of this

sample electrode When the density of the mixture layer of PVDF was measured with the graphite-grains child, it was 1.20 g/cm^3 and thickness was 96 micrometers. (002) and (110) a diffraction peak are measured for the obtained test electrode with X-ray diffractometer, and it is 7 from each peak top intensity. (002) The / (110) intensity ratio was measured. The result is written together to Table 1. 45 And 7 In the ** X diffraction, it was considered as X line source: CuK alpha rays /40kV/20 mA, and the step size of 0.02 degree. [0027]

The produced sample electrode was pierced in the size of 2-cm^2 , the constant current charge and discharge by 3 terminal method were performed, and measurement of charge-and-discharge capacity and a service capacity maintenance factor was performed as follows. The schematic diagram of the lithium secondary battery used for this measurement is shown in [drawing 2](#). Evaluation of a sample electrode, The solution which dissolved LiPF_6 in the beaker type glass cell 9 as the electrolysis solution 10 so that it might become the concentration of 1 mol/L at the mixed solvent of ethylene carbonate (EC) and methylethyl carbonate (MEC) (EC and MEC are 1:2 at a volume ratio) as shown in [drawing 2](#) is put in, The sample electrode 11, the separator 12, and the counter electrode 13 have been laminated and arranged, the reference pole 14 was further hung from the upper part, and the model cell was produced. Metal lithium was used for the counter electrode 13 and the reference pole 14, and the polyethylene micropore film was used for the separator 4. Between the sample electrode 11 and the counter electrode 13, the area of a sample electrode is received using the obtained model cell, It charges to 0V (V vs. Li/Li^+) by the constant current of 0.2 mA/cm^2 , the examination discharged to 1V (V vs. Li/Li^+) by the constant current of 0.2 mA/cm^2 is done, and it is 8. The service capacity per unit volume was measured.

100 cycle charge and discharge are repeated in a still more nearly similar way, and it is 9. The service capacity maintenance factor when service capacity of the first cycle eye was set to 100 was measured. It charges to 0V (V vs. Li/Li^+) by the constant current of 0.2 mA/cm^2 , The examination discharged to 1V (V vs. Li/Li^+) by the constant current of 6.0 mA/cm^2 was done, and the service capacity maintenance factor when service capacity when discharged by the constant current of (10) 0.2 mA/cm^2 was set to 100 was measured.

Each measurement result is written together to Table 1.

[0028]

Example 2

Except having made density of the mixture layer of PVDF into 1.45 g/cm^3 with the graphite-grains child by setting the pressure of a vertical press to 23MPa instead of 10MPa, The test electrode was produced by the same method as Example 1, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0029]

Example 3

Except having made density of the mixture layer of PVDF into 1.55 g/cm^3 with the graphite-grains child by setting the pressure of a vertical press to 31MPa, The test electrode was produced by the same method as

Example 1, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0030]

Example 4

Except having made density of the mixture layer of PVDF into 1.65 g/cm^3 with the graphite-grains child by setting the pressure of a vertical press to 50MPa, The test electrode was produced by the same method as Example 1, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0031]

Example 5

Except having made density of the mixture layer of PVDF into 1.75 g/cm^3 with the graphite-grains child by setting the pressure of a vertical press to 85MPa, The test electrode was produced by the same method as Example 1, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0032]

Example 6

Except having made density of the mixture layer of PVDF into 1.85 g/cm^3 with the graphite-grains child by setting the pressure of a vertical press to 143MPa, The test electrode was produced by the same method as Example 1, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0033]

Example 7

The jet mill ground Chinese natural graphite and scaly-natural-graphite particles were produced. This graphite-grains child's mean particle diameter, specific surface area, an aspect ratio, $d(002)$, and $Lc(002)$ measurement result are written together to Table 1. The test electrode was produced by the same method as Example 1 by setting the pressure of a vertical press to 2MPa using this graphite-grains child except having made density of the mixture layer of PVDF into 1.00 g/cm^3 with the graphite-grains child. By the same method as Example 1, (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm^2 were measured. A measurement result is written together to Table 1.

[0034]

Comparative example 1

Except having made density of the mixture layer of PVDF into 1.50 g/cm³ with the graphite-grains child by setting the pressure of a vertical press to 27MPa, The test electrode was produced by the same method as Example 7, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm² were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0035]
Comparative example 2

Except having made density of the mixture layer of PVDF into 1.65 g/cm³ with the graphite-grains child by setting the pressure of a vertical press to 42MPa, The test electrode was produced by the same method as Example 7, and (002)/(110) intensity ratio, the service capacity per unit volume, the service capacity maintenance factor after 100 cycles, and the service capacity maintenance factor at the time of discharge current 6.0 mA/cm² were measured by the same method as Example 1. A measurement result is written together to Table 1.

[0036]
[Table 1]

| (002) (Å) | 電極密度 (g/cm ³) | ×線回折強度比 (002)/(110) | 単位体積当り の放電容量 (mAh/cm ³) | 100サイクル 後放電容量 維持率(%) | 6.0mA/cm ² 放 電時の放電容 量維持率(%) |
|--------------|------------------------------|------------------------|---|----------------------------|--|
| 10以上 | 1.20 | 98 | 426 | 95 | 96 |
| | 1.45 | 126 | 516 | 94 | 93 |
| | 1.55 | 138 | 544 | 93 | 88 |
| | 1.65 | 170 | 574 | 89 | 85 |
| | 1.75 | 188 | 593 | 82 | 83 |
| 10以上 | 1.83 | 198 | 604 | 78 | 80 |
| | 1.00 | 205 | 361 | 91 | 92 |
| | 1.50 | 680 | 483 | 65 | 70 |
| | 1.65 | 835 | 497 | 50 | 43 |

| | 黒鉛種類 | 平均粒径 (μm) | 比表面積 (m^2/g) | アスペクト 比 | d(002) (Å) | $L_c(002)$ (Å) |
|-------|------|---------------------------|-----------------------------------|------------|------------|-------------------|
| 実施例 1 | 人造黒鉛 | 25 | 2.9 | 1.3 | 3.359 | 1000 \pm |
| 実施例 2 | | | | | | |
| 実施例 3 | | | | | | |
| 実施例 4 | | | | | | |
| 実施例 5 | | | | | | |
| 実施例 6 | | | | | | |
| 実施例 7 | 天然黒鉛 | 26 | 8.6 | 15 | 3.355 | 1000 \pm |
| 比較例 1 | | | | | | |
| 比較例 2 | | | | | | |

[0037]

As shown in Table 1, the negative electrode for lithium secondary batteries of this invention was high capacity, it excelled in a cycle characteristic and quick discharge characteristics, it used for the lithium secondary battery, and the suitable thing was shown.

[0038]

[Effect of the Invention]

According to this invention, the negative electrode for lithium secondary batteries excellent in a cycle characteristic and quick discharge characteristics is obtained, and it uses for the lithium secondary battery of high capacity, and is suitable.

[Brief Description of the Drawings]

[Drawing 1] an example of the lithium secondary battery of this invention is shown -- it is a section transverse-plane schematic diagram in part.

[Drawing 2] It is a schematic diagram of the lithium secondary battery used for measurement of charge-and-discharge capacity and a service capacity maintenance factor in the example of this invention.

[Description of Notations]

- 1 Anode 2 Negative electrode
- 3 Separator 4 Positive electrode tab
- 5 Negative electrode tab 6 Anode lid
- 7 Battery can 8 Gasket
- 9 Glass cell 10 Electrolysis solution
- 11 Sample electrode (negative electrode) 12 Separator
- 13 Counter electrode (anode) 14 Reference pole

[Translation done.]